



APPLICATION NOTE 08

ANALYTICAL SYSTEM FOR SUB-ppb MEASUREMENT OF SULFUR COMPOUNDS IN VARIOUS GAS MATRICES

The most reliable and user-friendly solution for ultratrace sulfur analysis in Hydrogen, Air and Carbon Dioxide

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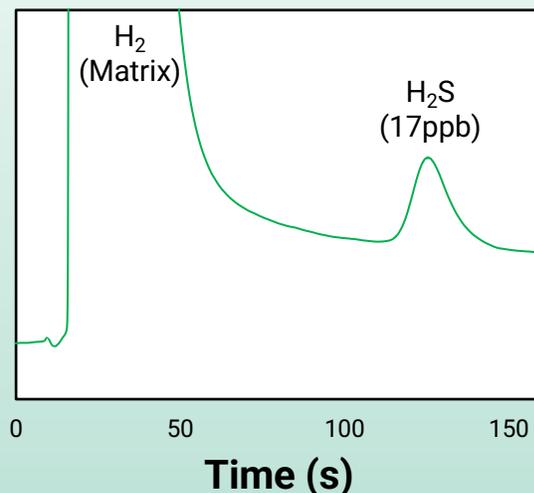
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ABSTRACT

Samples containing low-ppb levels of sulfur compounds in various matrices were generated with ASDevelop's intelligent gas calibration system (iGCS) to demonstrate the performance of the miniMOv GC platform equipped with a detector based on the Enhanced Plasma Discharge (Epd) technology. The samples were preconcentrated with ASDevelop's Sample Concentration System (SCS), which uses our proprietary trapping material for sulfur and unique Trap & Release purged lip sealing valve (T&R PLSV). The method developed with this system was demonstrated to be reliable and sensitive enough for real-life application with various gas matrices containing ppb and sub-ppb level sulfur compounds. A limit of detection (LOD) of 100 ppt was calculated for H₂S in hydrogen (H₂), air and carbon dioxide (CO₂). Its LOD can be further improved to 35 ppt thanks to the unique enhanced LOD (eLOD) algorithm implemented in the miniMOv software. The system developed by ASDevelop offers many benefits compared to systems using Sulfur Chemiluminescence Detectors (SCD) and Flame Photometric Detectors (FPD).



Introduction

The reduced sulfur compounds are key impurities often found in various gas matrices. This family of compounds includes hydrogen sulfide (H₂S), carbon disulfide (CS₂), carbonyl sulfide (COS), methylmercaptan (MeSH), dimethyl sulfide (DMS), dimethyl disulfide (DMDS), as well as other less common organosulfurs. Sulfur compounds are key impurities found in fuel-grade hydrogen. Indeed, the natural gas used for hydrogen generation by steam methane reforming often contains sulfur compounds [1], which could end-up in the final product. There are also studies on the possibility of transporting hydrogen in natural gas pipelines. The hydrogen transported with this method will most likely have to undergo a de-sulfurization process, due to the presence of various sulfur compounds in these pipelines [2]. It was shown that these molecules can be irreversibly adsorbed on electrodes and cause permanent degradation of the fuel cell performances. Therefore, the current ISO standard (ISO FDIS 14687-2) for fuel-grade hydrogen limits the total sulfur concentration to 4ppb. However, even at such low concentration, the sulfur compounds still affect the performances of the fuel cells, and it was

recommended to reduce the maximum limit of total sulfur in fuel-grade hydrogen down to 2 ppb or even lower [3].

Due to their bad odor and potential health hazards, many jurisdictions implemented very strict environmental quality standards to limit the concentration of sulfur compounds in air. While the standard varies from one jurisdiction to another, the concentration of each sulfur compound is typically limited to the low-ppb level [4]. Furthermore, the World Health Organization (WHO) recommends that ambient H₂S levels not exceed 5 ppb for a 30 minute period [5].

Monitoring of sulfur compounds is also extremely important in the field of food-grade gases, especially CO₂. This gas is often used for carbonation of beverages and food preservation, as it is relatively inert and has no distinctive taste or odor. However, CO₂ is produced from various chemical processes and sulfur compounds are often obtained as side products. Therefore, food-grade CO₂ must undergo multiple purification steps to remove undesirable impurities. Due to the distinctive taste and odor of the sulfur compounds, the International Society of Beverage Technologists (ISBT) Carbon Dioxide Guidelines

limits total sulfur concentration to 0.1 ppm v/v [6].

Current state of the art in sulfur analysis

To meet the environmental regulations or assess the high purity of fuel-grade hydrogen, highly sensitive instruments must be used. The Sulfur Chemiluminescence Detectors (SCD) is currently one of the most widely used detector for such applications thanks to its good selectivity for sulfur and high sensitivity [7]. However, this technology also suffers from many drawbacks. Indeed, to be detected, the sulfur compounds must undergo a series of highly sensitive chemical reaction in a high-temperature furnace or a hydrogen-air flame and with ozone in a separated chemiluminescence chamber. Sulfur is quantified by measuring the resulting light emission. These reactions are highly sensitive to the presence of moisture and the excess ozone must be trapped due to its high toxicity. Multiple traps must therefore be used, and they must often be changed for optimal performance. Furthermore, the response of the detector strongly depends on the position and condition of a ceramic probe located after the furnace or the hydrogen-air flame. This probe must often be cleaned and conditioned to remove the impurities, which often leads to unreliable quantification. This results in a costly detector with important down time for frequent maintenance and it must be operated by highly-skilled specialists [8]. Laboratories have already started to replace costly SCD with our solution.

The Flame Photometric Detector (FPD) is a simpler and more affordable alternative to the SCD. This detector is similar to the Flame Ionization Detector (FID), but measures light emission from the sulfur compounds in a hydrogen-air flame with a photomultiplier tube equipped with an optical filter centered at 394nm. Since the FPD measures light emission from the S_2 radicals that are formed in the flame, the detector output is not linear. It is proportional to the square of the sulfur mass flow rate [8]. The FPD is also much less sensitive than SCD, with a LOD in the order of 50 ppb for most compounds. Better LOD can be achieved with a Pulsed FPD (PFPD), but this detector is much more

complicated to operate, as it requires two different combustible gas flows and a gated amplifier to record specific components of each pulse.

Over the past years, ASDevelopments released the SePdd, a detector based on the Enhanced Plasma Discharge (Epd) patented technology. Results previously acquired with this detector demonstrated that reduced sulfur compounds in hydrogen can all be measured with a limit of detection below 5 ppb without sample preconcentration and 1 ppb using enhanced limit of detection (eLOD) signal treatment algorithm available in ASDevelopments' ASDSense software [10-12]. This detector only requires a low helium flow (<20mL/min) as the carrier and discharge gas. Reduced sulfur compounds have also been measured using argon or nitrogen as the carrier/discharge gas, resulting in lower operation costs, but also slightly lower sensitivity. There is no need for any additional UHP gases for fueling the detector or chromatographic system. To further improve the limit of detection for the reduced sulfur compounds, the SePdd was integrated in our newly released MiniMOv GC platform, equipped with our Sample Concentration System (SCS). In combination with our Intelligent Gas Calibration System (iGCS) to generate low-concentration sulfur standards, we were able to demonstrate that this system can be used to measure sub-ppb level of sulfur compounds in various matrices.

Experimental Information

The results presented in this document were acquired with a system that only uses ASDevelopments components: SePdd detector, miniMOv GC platform, as well as our PLSV valves, purged electronic gas flow controllers, high-quality electronics, software, tubes and fittings. The use of other components will not lead to the same performance. The overall is not only due to a single component, but to the combination of all of them. For example, even with our highly sensitive detector for reduced sulfur compounds, using lower-quality components such as GC valves, gas flow controllers and fittings could lead to a noisier baseline and therefore much less sensitive measurements.

Standard gas generation with the iGCS



Figure 1 – ASDevices' intelligent Gas Calibration System (GCS) used for standard gas dilution

First of all, it is important to explain how the standard gases used for this test were generated. Two samples containing sulfur compounds were used: one with 56.1 ppm H₂S, 53.5 ppm COS, 49.9 ppm CS₂, 60.6 ppm MeSH, 35.5 ppm DMS and 30.8 ppm in nitrogen and another with 37.5 ppm H₂S, 51.2 ppm CS₂, 50.4 ppm DMS, 73.7 ppm MeSH and 28.7 ppm DMDS in helium (Messer Canada). These samples were diluted in various high-purity matrices, from tens of ppb down to the low-ppb level, with the intelligent Gas Calibration System (iGCS), presented in Figure 1. This dilution system is based on a NIST-traceable laser-calibrated orifice technology (see Figure 2), allowing for greater dilution ratio flexibility and better precision than traditional mass flow type systems. Indeed, this orifice technology allows better control on the dilution by maintaining the gases in the sonic regime. This is especially important for this application, since different gases are mixed together. In the sonic regime, the gas flow through the orifice is a function of the inlet pressure alone – it is not influenced in any way by the outlet pressure. Therefore, two different gas flows should perfectly blend regardless of their nature. In the sub-sonic regime, mixing two different gas matrices can lead to important errors on the dilution.



Figure 2 – NIST-traceable stainless-steel gasket with laser-drilled sonic orifice used in the GCS

Indeed, in order to maintain a stable dilution, the orifice temperature and the inlet pressure of both gases must also be stable. This is why the orifices were maintained in a heated enclosure at 40°C. The inlet pressure is insured by the use of our high-precision electronic pressure controllers (EPC).

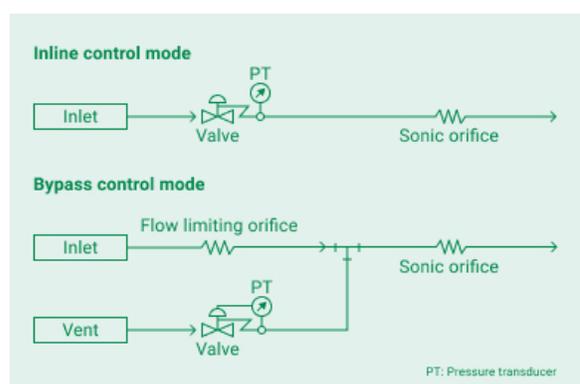


Figure 3 - Inline (above) and Bypass (below) pressure controller configurations for gas flow control.

All the components, including the tubing, fittings and orifices in contact with the sample were sulfonert-treated to avoid losses of the sulfur compounds. The matrix gas (H₂, Air, CO₂) flow was controlled using the inline configuration, as presented in Figure 3, since these gases do not contain any reactive analytes. The purged enclosure of the EPC allows good conservation of the matrix gas integrity by preventing leaks from ambient air. A 150 µm orifice was used to control the matrix, allowing flow rates in the sonic regime between 1L/min and 5.5L/min for hydrogen and between 400mL/min and 1.2L/min for the other matrices. For the sample containing sulfur compounds, a bypass configuration was used instead, due to the high reactivity of the sulfur compounds and the presence of mechanical parts in the EPC. This configuration increases gas consumption but allows a much better sample integrity for reactive analytes. A 5 µm orifice was

used to control the sample, allowing flow rates in the sonic regime between 0.5mL/min and 5mL/min. The outlet pressure was maintained between 5 and 9 PSI, depending on the matrix gas. The outlet pressure had to be maintained low enough to allow the broadest sonic range possible, while allowing a good sample flow rate through the trap of the sample concentration system.

miniMOV GC Platform and Sample Concentration System



Figure 4- ASDevices' miniMOV GC platform with the sample concentration system (SCS)

The miniMOV is the latest benchtop GC platform released by ASDevices (Figure 4). It benefited from our three decades of expertise in designing robust and reliable process-oriented instruments for the analysis of ultra-high purity gases in the field of semiconductors, air separation and other specialty gases. The miniMOV contains one ramping oven and one isothermal oven. The platform can be equipped with up to 10 purged EPC, 3 valves and two detectors. It was optimised for the use of ASDevices' detectors (SePdd, eFID, FePID and TCD), but it is also compatible with

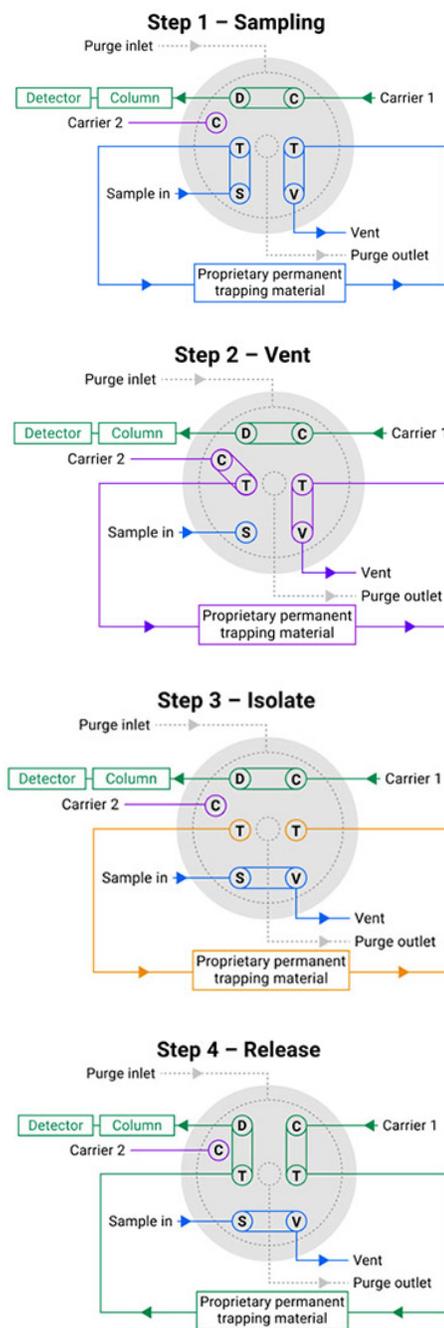


Figure 5 – The T&R PLSV and its four configurations

almost any other third-party detector. It can be used with packed, μ packed and capillary columns. A sample concentration system (SCS) based on thermal desorption and an auto-sampler are also available in option.

The SCS is designed around our patent-pending Purged Lip Sealing Valve (PLSV) Trap & Release (T&R) technology, with its unique configurable 4-

steps process that ensures sample integrity. This allows sampling, matrix venting, trap isolation and trap release with a single leak-tight valve. Figure 5 presents these four configurations.

Indeed, the main drawback associated with most thermal desorption systems currently available on the market is their poor leak integrity, especially due to the valves and trap holder. This is especially important for the analysis of ultra-trace level impurities, as contamination from air could cause interference. A good leak integrity also prevents from side-reactions with oxygen or water and protects the GC column from contamination that could build-up in the long-term. Therefore, a new type of holder was designed for the SCS, based on our extensive expertise in the field of ultra-trace analysis, specifically to ensure leak integrity of the traps. Furthermore, the PLSV valve technology, which will be covered in the next section, also offers unequalled leak integrity. By combining all the steps required for T&R in a single valve, this further limits the risks of leaks from a faulty valve. Indeed, typical T&R systems usually rely on multiple valves to do the same task. Another drawback of systems that use multiple valves is the significant dead volume that comes with such configuration. With a single T&R PLSV, the dead volume is reduced to its minimum.

Thanks to the temperature control system the trap temperature can be precisely controlled between -30°C and 300°C, allowing good adsorption of the most volatile molecules and release of the most adsorbed, for a broad range of applications.

PLSV valve technology^{patent-pending}

The PLSV is a unique valve technology developed by ASDevelopments, which offers many advantages over the other chromatographic valve technologies [13-15]. For ultratrace sulfur analysis, it is necessary to treat the valve head with an inert treatment. Due to the sealing force required in typical conical rotary valves, such treatment cannot be used, as it would cause treatment peeling after only a few actuations. With the PLSV technology, thanks to its reduced surface sealing area and reduced sealing force, sulfur-inert-treated valves can be used for more than 500 000 actuations without peeling. For

untreated valves, their lifetime can even go up to 1 000 000 actuations for use in UHP gasses analysis. The PLSV technology also uses a unique purge system, presented in Figure 6, which makes leaks virtually impossible. Indeed, small molecules like hydrogen and helium have a strong tendency to leaks between ports, but it can be prevented with this purge. Furthermore, the purge protects the sample integrity from outboard leaks, which is especially important for the preconcentration and measurement of ultra-trace level impurities. The PLSV technology has been implemented in the 6, 10 and 14 ports valves used in the miniMOv platform as well as the T&R valve developed for the SCS.

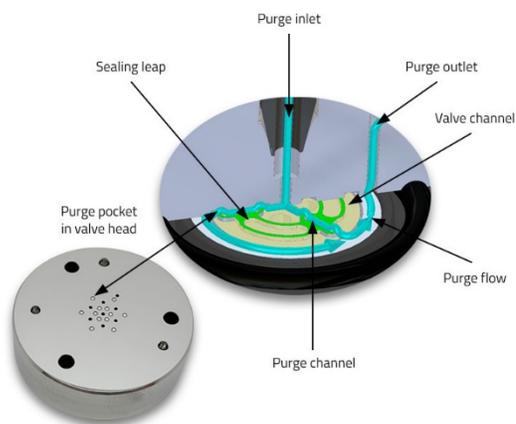


Figure 6 – PLSV Technology principle

SePdd Detector^{patented}

All the measurements presented in this document were done with the SePdd (see Figure 7). This detector is based on the Enhanced Plasma Discharge (Epd) technology developed by ASDevelopments. Due to its versatility, ease of use, low maintenance cost, robustness and high sensitivity to sulfur compounds, the Epd



Figure 7 - The SePdd detector

technology is an excellent alternative to SCD, FPD/PFPD and mass spectrometry (MS) for sulfur measurement on most GC systems. Indeed, with its highly energetic stabilised and focused plasma discharge, the sulfur compounds are easily ionised and measured by monitoring specific wavelengths emitted from the plasma. It can be operated with helium, argon or nitrogen as the carrier gas. Since the carrier gas used for chromatography is also used as the plasma discharge gas, there is no need for any additional UHP gas to operate the detector. Furthermore, there are no safety hazards caused by a flame or a heated furnace. The sensitivity of the detector is further increased thanks to the presence of electron-injection and stabilising electrodes, which significantly improve the ionization efficiency and decrease the background noise. The Epd principle is presented schematically in Figure 8.

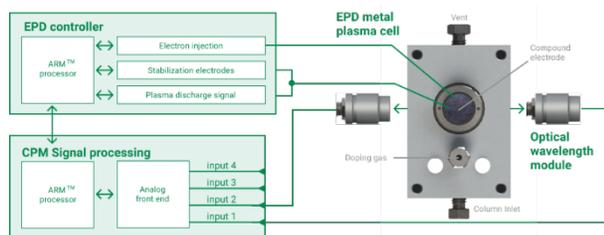


Figure 8 – Epd principle

Signal Processing

The proprietary platform-embedded GC software and Chromatographic Processing Module (CPM) integrate very advanced signal processing

methods, which are unique to ASDevices. The CPM can simultaneously acquire and combine up to 4 signals from different wavelengths or detectors. This allows unique measurement modes such as the Spectral Compensation, which is presented in TN-05 [16]. For the current application, only a single wavelength is showed. Other configurations that will even push the performance further are possible. These will be covered in the next publication on this topic.

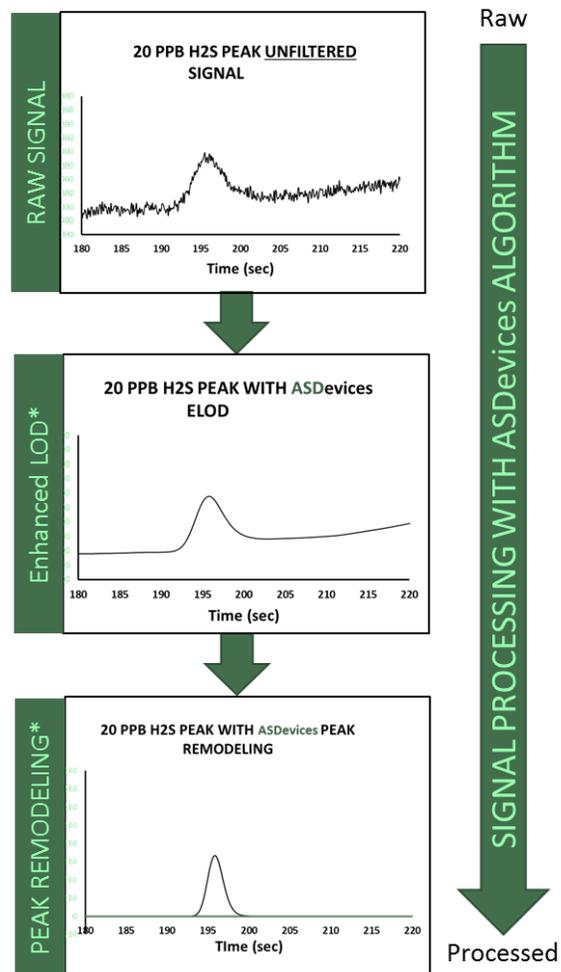


Figure 9 – ASDevices' peak processing step by step. LOD and repeatability are improved with each processing step. These results were acquired without sample preconcentration.

The GC software also offers two unique proprietary advanced signal processing algorithms: the enhanced LOD (eLOD) and Peak Remodeling (Figure 9). The eLOD algorithm analyses and learns the detector baseline noise

and peak shape overtime based on a number of consecutive chromatograms defined in the software. The learning process allows to better understand the power distribution of the signal and differentiate between noise and a meaningful signal from an analyte. This advanced principle based on artificial intelligence allows to recover the peak shape in a noisy signal. Signal to Noise ratio (SNR) improvement between 3 and 10 times can be achieved. The final processing step is the peak remodeling which, based on raw peak shape, remodels the peak into a gaussian shape while keeping the area constant. This improves peak integration and the overall result is an improved LOD.

GC Method

For most tests presented in this document, the miniMOv GC platform and SCS were configured as presented in Figure 10 (above). The detector inlet, as well as all the valves, tubes and unions in contact with the sample were sulfinert-coated to avoid losing the traces of highly reactive sulfur compounds by adsorption on the various components. As in the iGCS dilution system, the sample gas is controlled in bypass configuration to ensure sample integrity. The carrier gas flows are controlled in inline configuration, since they contain no sulfur. For optimal performances, the carrier gas was purified using ASDevices' ASDPure purifier, which removes trace of permanent gases (H₂, O₂, N₂, CH₄, CO, CO₂) and water down to 1 ppb. The diluted sample generated with the iGCS is directed to the system via the sample inlet of the SCS.

The SePdd detector is connected to a permeation tube via the doping port. This is used for doping the plasma with water, as it helps plasma stabilisation and generate new emission wavelengths, which are measured for sulfur quantification. The carrier gas flow through the permeation tube was set to 5mL/min.

The SCS was equipped with a trap that contains ASDevices' proprietary trapping material developed for the preconcentration of reduced

sulfur compounds in various gas matrices. It requires a sampling temperature of -30°C and a release temperature of 210°C. Before the tests, the material is regenerated for one hour at 230°C. The trap is also cleaned at 230°C for 4 minutes between each analysis to avoid interference from other impurities that would stick to the trap. The sample gas flow was set to 150mL/min through the trap and the carrier gas flow for venting was set to 25mL/min. Here, only splitless injection was used.

The miniMOv platform was configured with a 1m x 1mm Rt-XLSulfur micropacked GC column (Restek), as shown in Figure 10 (above). This column was selected, as from our experience, it offers very robust, accurate and fast results for the analysis of reduced sulfur compounds. However, DMS and CS₂ are co-eluting on this column. Therefore, another configuration using a 30m x 0.320mm GS-GasPro and a 40m x 0.320mm DB-Sulfur capillary columns (Agilent) in a heartcut configuration was also tested to demonstrate the preconcentration capabilities of both DMS and CS₂ as presented in Figure 10 (below).

**** IMPORTANT NOTE ON FERRULES****

Graphite ferrules should not be used for sealing capillary columns and tubes, as they are permeable to oxygen. While this is acceptable for low-sensitivity detectors like TCDs and FIDs, oxygen leaks could cause interference while measuring at the ultra-trace level. Therefore, we strongly recommend the use of Graphite / Vespel Polyimide ferrules for sealing capillary columns and capillary tubes, since this type of ferrule is not permeable to oxygen [17]. Here, 40% Graphite / 60% Vespel Polyimide ferrules (Chromatographic Specialties) were used, but different blends are available depending on the distributor. The use of SilTite metal ferrules could also be considered, as it should offer adequate sealing. Regular stainless-steel ferrules can be used for packed and micropacked columns.

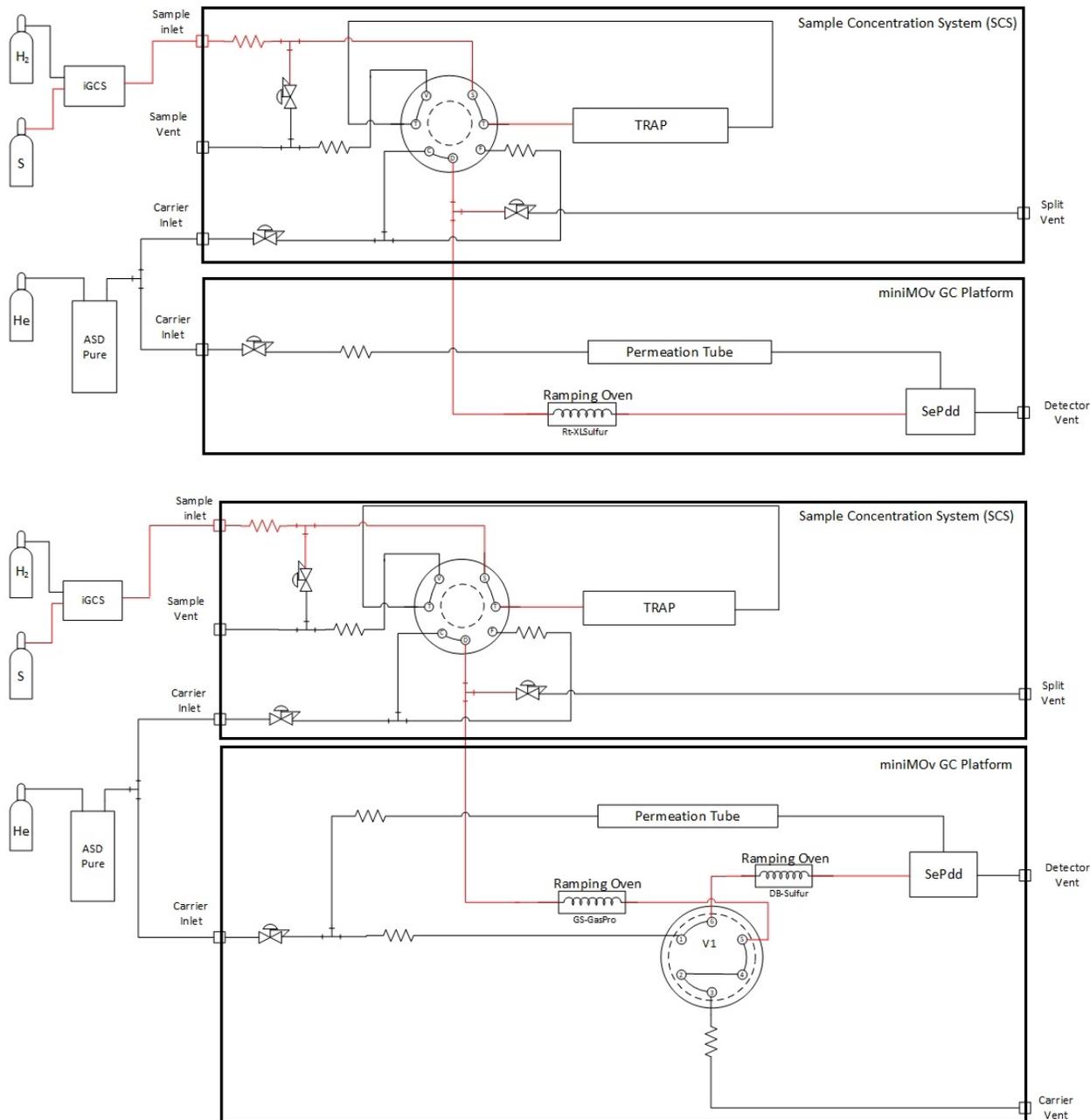


Figure 10 – Configurations of the miniMOv GC platform with the Sample Concentration System for sulfur preconcentration and measurement. The system above uses a single Rt-XLSulfur GC column, while the system below uses two capillary columns and a heartcut valve. The red lines represent the sulfinit-coated tubes.

For sample preconcentration, the following sequence was followed for all the matrices. Refer to Figure 5 for the different valve configurations:

- 1) Sampling at -30°C , typically for 240 seconds.

The sampling temperature is a very important parameter. When sampling is done at higher temperature – even at -20°C – H₂S is not well retained by the trapping material. This highlights the importance of using a preconcentration system that can manage such low temperature. The effect of the

sampling time will also be presented in the Results and Discussion section. Here, we mostly used 240 seconds sampling time, as it offers a good compromise between time and sensitivity, but the sensitivity of the method can be significantly improved by increasing the sampling time.

- 2) Matrix venting at -30°C for 10 to 600 seconds.

Venting is a really important step, as it removes most of the matrix, which could interfere or react with the chromatogram baseline. With a venting flow of 25mL/min, a significant amount of all matrices was removed after only 10 seconds on our proprietary trapping material. Longer venting times were also tested and could be beneficial depending on the matrix. It was shown that even after 10 minutes venting at -30°C, all the sulfur compounds, including H₂S, remain on the trapping material without any noticeable loss. The T&R PLSV is the only valve equipped with an integrated feature for trap venting. Typical preconcentration systems would require 2 valves or more to achieve this step.

- 3) Desorption (Release configuration) at 210°C for 500 seconds.

During this step the trap is inline with the chromatographic columns and detector. Therefore, any leak or temperature variation on the trapping system would have a significant impact on the chromatogram and detector response. Therefore, the level of leak integrity and precise temperature control that can only be achieved with ASDevices' SCS is especially important.

- 4) Trap purge at 230°C for 240 seconds.

This final purge step is optional, but allows removal of impurities that could remain on the trap and cause interferences in subsequent analysis.

Between each analysis, the trap is maintained in isolated position to avoid trap contamination.

Helium was used as the carrier / discharge gas. For the first configuration (Figure 10 above) –

with only one Rt-XLSulfur micropacked column – the helium flow rate was set to 25mL/min and the temperature ramp was set from 40 to 250°C at a rate of 30°C/min after sample release.

For the second configuration (Figure 10 below) - with the two capillary columns - the ramping oven temperature was set from 40°C to 250°C at a rate of 15°C/min after sample release. The second column was put inline with the rest of the system using the heartcut valve only 350 seconds after sample injection. This was to remove most of the remaining matrix gas, which elute faster than the sulfur compounds. The flow was set to 5mL/min, but was increased to 15mL/min 540 seconds after sample injection. This was because of the good separation between each sulfur compound peak and to reduce the long elution time for the heavier compounds.

Results and Discussion

Sulfur preconcentration in hydrogen

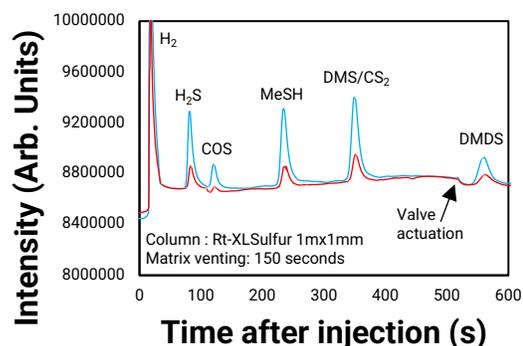


Figure 11- Chromatograms acquired for 41.2 ppb H₂S, 42.7 ppb COS, 39.8 ppb CS₂, 48.4 ppb MeSH, 28.2 ppb DMS and 24.6 ppb DMDS in hydrogen (Blue line) and for 10.3 ppb H₂S, 10.6 ppb COS, 10.0 ppb CS₂, 12.1 ppb MeSH, 7.1 ppb DMS and 6.2 ppb DMDS in hydrogen (red line)

First, the iGCS was set to generate a diluted sample containing 41.2 ppb H₂S, 42.7 ppb COS, 39.8 ppb CS₂, 48.4 ppb MeSH, 28.2 ppb DMS and 24.6 ppb DMDS in hydrogen, which is a dilution ratio of 1:1250. Another sample containing 10.3 ppb H₂S, 10.6 ppb COS, 10.0 ppb CS₂, 12.1 ppb MeSH, 7.1 ppb DMS and 6.2 ppb DMDS in hydrogen (1:5000) was also generated. The

miniMOv platform was configured with a Rt-XLSulfur column, as shown in Figure 10. The sampling time was set to 240s at 150mL/min, while the trap was cooled down to -30°C. Here, the matrix venting was set to 150 seconds. The chromatograms acquired are presented in Figure 11. More results concerning the signal linearity as a function of the sample concentration and sampling conditions using this configuration will be presented in a following section.

The result presented here show that all the sulfur compounds analysed were successfully preconcentrated on ASDeVICES' proprietary material for sulfur in hydrogen. From these results, LODs of 100 ppt for H₂S, 750 ppt for COS, 230 ppt for MeSH, 250 ppt for DMS/CS₂ and 270 ppt for DMDS were calculated. Note that the baseline variation at 500 seconds is due to the T&R valve actuation, from the "release" to the "purge" position.

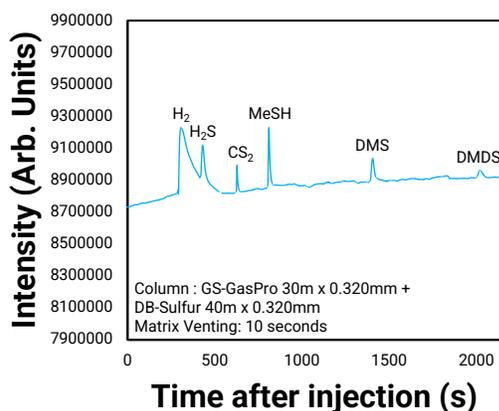


Figure 12 - Chromatogram acquired for 14.9 ppb H₂S, 20.4 ppb CS₂, 29.5 ppb MeSH, 20.1 ppb DMS and 11.4 ppb DMDS in hydrogen.

Due to the co-elution of DMS and CS₂ on the Rt-XLSulfur column, we also tested a setup using a GS-GasPro and DB-Sulfur capillary columns, to confirm that both compounds are indeed well preconcentrated. For this test, the iGCS was set to generate a diluted sample containing 14.9 ppb H₂S, 20.4 ppb CS₂, 29.5 ppb MeSH, 20.1 ppb DMS and 11.4 ppb DMDS in hydrogen. The chromatogram acquired with this configuration is presented in Figure 12. Here, a sampling of 240

seconds at 150mL/min was also used, but the matrix was only vented for 10 seconds.

The results obtained here show that both DMS and CS₂ are indeed well preconcentrated on ASDeVICES' proprietary trapping material. The LOD calculated using this method is 110 ppt for H₂S, 185 ppt for CS₂, 125 ppt for MeSH, 220 ppt for DMS and 330 ppt for DMDS. While the LOD is slightly better for some analytes using this configuration, the configuration using Rt-XLSulfur micropacked column was preferred, due to its faster analytical time. Still, this configuration was used to determine the linearity and effect of the sampling volume for H₂S, CS₂, MeSH, DMS and DMDS, which will be presented in a following section. Note that these LODs were calculated without using the eLOD feature of the miniMOv software. The impact of the eLOD will also be presented in a following section.

Repeatability

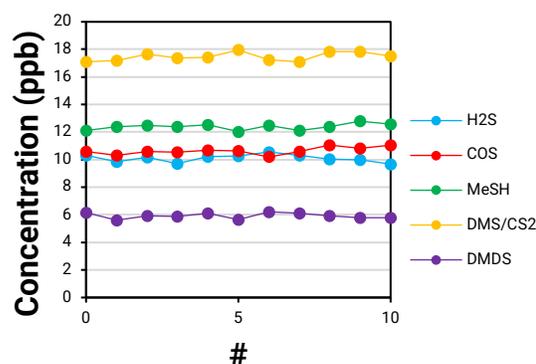


Figure 13 - calculated concentration (ppb) for sulfur compounds in hydrogen in 10 consecutive runs after system calibration.

The repeatability was determined by measuring 10 consecutive samples generated using the iGCS, always with the same dilution ratio in hydrogen. These 10 chromatograms were acquired after the system was calibrated (Analysis #0). The concentration of each analyte was then determined from peak integration by the software. The timing of each peak was determined from previous runs and was manually inputted in the ASDSense software before calibration. The calculated concentrations are presented in Table 1 and Figure 13.

Table 1 – Calculated concentration (ppb) for sulfur compounds in hydrogen in 10 consecutive runs after system calibration

#	H ₂ S	COS	MeSH	DMS/CS ₂	DMDS
0	10.3	10.6	12.1	17.1	6.15
1	9.86	10.3	12.4	17.2	5.61
2	10.2	10.6	12.5	17.6	5.93
3	9.71	10.6	12.4	17.4	5.88
4	10.2	10.7	12.5	17.4	6.09
5	10.3	10.6	12.0	18.0	5.66
6	10.6	10.2	12.5	17.3	6.22
7	10.3	10.6	12.1	17.1	6.10
8	10.0	11.1	12.4	17.8	5.92
9	9.97	10.8	12.8	17.8	5.78
10	9.68	11.0	12.6	17.5	5.80
Avg.	10.1	10.6	12.4	17.5	5.92
σ	0.27	0.26	0.23	0.31	0.20
Rep.(%)	2.7	2.4	1.8	1.8	3.4

It is important to consider that the variation in the results is caused by multiple components: the iGCS dilution system, the SCS preconcentration system and the chromatography itself. Therefore, the excellent repeatability obtained highlights the importance of using high-quality components, as each of them might have a significant impact on the results.

Enhanced LOD (eLOD) algorithm

Our ASDSense GC software integrates advanced signal processing algorithm which can be used to improve the method limit of detection (MDL). The method limit of detection is different than the limit of detection of the detector. The MDL takes into consideration, not only the detector performance, but all the components (columns, valves, baseline shape) to assess the real performance of the instrument.

Our most advanced algorithm is known as eLOD (enhanced Limit of Detection). The power of this method resides in its ability to learn from the instrument noise and improve the limit of detection while preserving the peak shape as shown in Figure 14, which is very important in chromatography. The learning process allows to better understand the power distribution of the signal and differentiate between noise and a meaningful signal from an analyte. Many filtering algorithms, such as moving or rolling average,

indeed reduces the noise, but also reduces peak height and increases peak broadening.

Figure 14 shows a raw chromatogram obtained with our Epd sensing technology (Blue line) for 700 ppt MeSH and 860 ppt DMS/CS₂ in hydrogen generated with the iGCS. The resulting eLOD chromatogram with a learning parameter of 8 cycles (Red line) is shown, as well as a chromatogram filtered with a moving average (Black line) for comparison. The advantage of the eLOD algorithm is clear. The peak height, retention time and shape are preserved while the signal to noise is greatly improved. Another benefit of our algorithm that is clearly demonstrated here is related to peak broadening. From Figure 14, the MeSH peak filtered with moving average becomes much broader and even coelutes with a small peak which is just after.

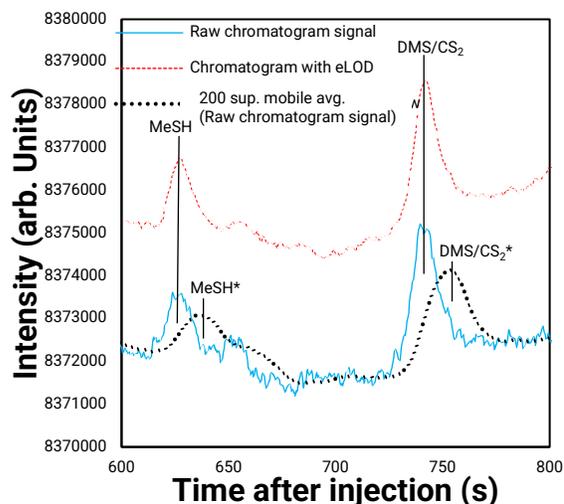


Figure 14 – Chromatograms acquired for 700 ppt MeSH and 860 ppt DMS/CS₂ without eLOD (Blue line), with eLOD (Red line) algorithm and with a moving average (Black line)

The full benefits of that algorithm occur when the instrument continuously measures a sample from the same source, such as an H₂ sample from an industrial manufacturing process. The continuous analysis allows the algorithm to properly learn from the instrument signal and provide the best signal to noise enhancement. The eLOD algorithm can improve the Limit of detection by a factor between 3 and 10 times. In

addition to that, the filtered chromatogram is easier to process by the peak detection algorithm which result is better repeatability. In regard to Figure 14 chromatogram, the LOD was improved by a factor of 3 resulting in a LOD of less than 70 ppt for MeSH and DMS/CS₂. For H₂S, the LOD was improved to 35 ppt thanks to the eLOD algorithm. The LOD calculation is based on the method described in our application note “Not all LOD are the same”.

Sulfur Preconcentration in Air

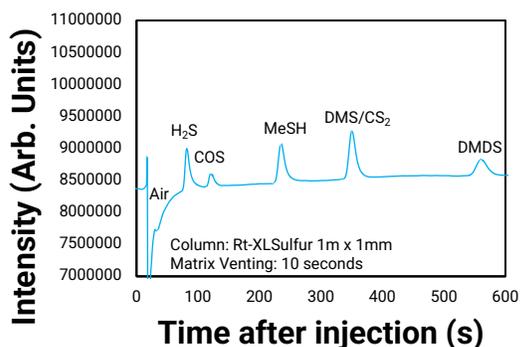


Figure 15 - Chromatogram acquired for 42.9 ppb H₂S, 44.5 ppb COS, 50.4 ppb MeSH, 29.3 ppb DMS, 41.5 ppb CS₂ and 25.6 ppb DMDS in air after 240s sampling at 150mL/min with 10s matrix venting using a Rt-XLSulfur GC column

Then, a sample containing 42.9 ppb H₂S, 44.5 ppb COS, 50.4 ppb MeSH, 29.3 ppb DMS, 41.5 ppb CS₂ and 25.6ppb DMDS in air was generated with the iGCS. Here, the same sampling conditions were used as previously and with a matrix venting time of 10 seconds. Indeed, only 10 second matrix venting was required, as air has almost no affinity with ASDevices’ proprietary trapping material for sulfur. However, as it will be presented in a following section, it is essential to remove as much air as possible before heating the trap, since it can react with some of the trapped components. Here, the LODs are similar to the ones calculated in hydrogen matrix, with a LOD of 100 ppt for H₂S, 650 ppt for COS, 245 ppt for MeSH, 290 ppt for DMS + CS₂ and 310 ppt for DMDS. This shows that this system is also highly efficient for trapping the sulfur compounds in air. The chromatogram acquired is presented in Figure 15.

Note that a better separation between the air matrix and H₂S can be achieved by starting column temperature ramping after H₂S elution, but the result obtained here was considered satisfactory as it allows good H₂S quantification and a faster cycle time.

Sulfur Preconcentration in CO₂

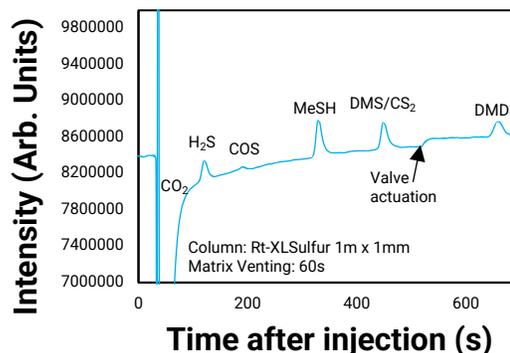


Figure 16 - Chromatogram acquired for 30.3 ppb H₂S, 31.4 ppb COS, 35.6 ppb MeSH, 20.7 ppb DMS, 29.3 ppb CS₂ and 18.1ppb DMDS in CO₂ after 240s sampling at 150mL/min with 10s matrix venting using a Rt-XLSulfur GC column

Finally, a sample containing 30.3 ppb H₂S, 31.4 ppb COS, 35.6 ppb MeSH, 20.7 ppb DMS, 29.3 ppb CS₂ and 18.1 ppb DMDS in CO₂ was generated with the iGCS and analyzed with the miniMOv system, as presented in Figure 16. The sampling conditions are the same as previously presented, but with a matrix venting time of 60 seconds to remove enough CO₂ before releasing the sample. Similar LODs as for other matrices were calculated for H₂S (190 ppt), MeSH (290 ppt) and DMDS (290 ppt). However, the signal for COS (4ppb LOD) and DMS/CS₂ (530 ppt LOD) was much lower. Preliminary results acquired with a DB-Sulfur and GS-GasPro capillary columns show that CS₂ preconcentration was significantly affected by the CO₂ matrix, while DMS was not. This could be explained by the fact that CO₂, COS and CS₂ have a similar chemical structure and therefore, they are competing for the same active sites on the trapping material. Since CO₂ concentration is much higher than CS₂ or COS, the analytes are “pushed” out of the trapping material by the CO₂. Still, the results acquired show that H₂S, MeSH,

DMS and DMDS are well retained on ASDevices' proprietary trapping material for sulfur, even in CO₂ matrix. It is noteworthy that even without sample preconcentration, all these compounds, including COS and CS₂, can be measured down to the low-ppb level using the miniMOv or iMOv GC platform coupled with the SePdd [10-12], which should be enough to analyze food-grade CO₂, which only require total sulfur compounds below 0.1 ppm v/v [6]. Still, for the analysis of sub-ppb level CS₂ and COS, new trapping materials will have to be developed.

Matrix Venting

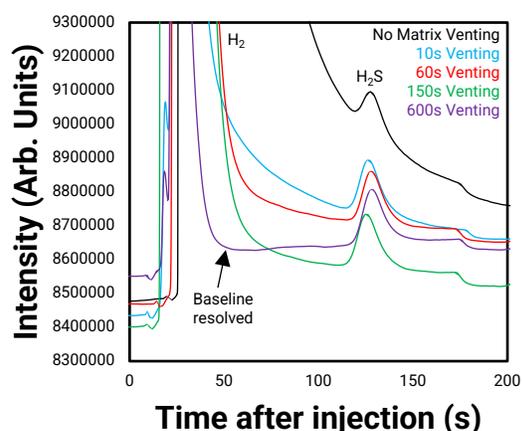


Figure 17 - Chromatograms acquired for 17ppb H₂S in hydrogen without matrix venting (Black Line) and with 10s matrix venting (Blue Line), 60s matrix venting (Red Line), 150s matrix venting (Green Line) and 600s matrix venting (Purple Line)

Matrix venting is a critical step for the analysis of a pre-concentrated sample. Our 30 years of expertise has thought us to avoid all possible interferences, whether the detector is sensitive or not to the matrix. At ultra-trace level, everything matter. Indeed, without venting, the matrix could co-elute with some analytes. For example, even with a heartcut, it can be difficult to fully separate H₂S from the hydrogen matrix. Furthermore, due to their reactivity and small size, hydrogen molecules have a strong tendency to stick to most trapping materials used in thermal desorption systems, especially at very low temperature. Figure 17 presents the effect of

matrix venting time for the preconcentration of a sample containing 17 ppb H₂S in hydrogen.

The results presented in Figure 17 were all acquired with a sampling time of 240 seconds at 150mL/min and only using a single 1m x 1mm Rt-XLSulfur micropacked GC column, without heartcut. The helium flow rate for venting was set to 25mL/min. The trap temperature was maintained at -30°C during venting. Without matrix venting, the H₂S peak is co-eluting with the hydrogen matrix and would require a heartcut to be properly separated. After only 10 seconds venting, most of the hydrogen is removed, but there is still some hydrogen co-eluting with the H₂S peak. 150 seconds venting was required to obtain a well-separated H₂S peak. Here, we tested up to 600 seconds matrix venting time, but due to its high reactivity, some hydrogen remains adsorbed to the trap. Still, this long venting time did not cause any H₂S desorption. This highlights the high performance of the proprietary material developed by ASDevices for the preconcentration of sulfur compounds. Indeed, H₂S is well known for being weakly adsorbed on most commercially-available trapping materials, but is well retained here.

Another problem to consider is the chemical reactivity of the matrix with the analytes. Indeed, samples are typically released from the trap at high temperature, above 200°C. While most matrix gases are inert at low temperature, chemical reactions can be initiated at higher temperatures before the sample is released. A good example is the chemical reaction of the oxygen from air with H₂S and COS, as presented in Figure 18.

When air is not vented, the signal from H₂S is significantly reduced, while COS is completely eliminated. However, the H₂S and COS peaks can be fully recovered with only 10 seconds matrix venting at 25mL/min before heating the trap. Therefore, matrix venting is an essential step, especially when preconcentrating reactive analytes in reactive matrices. This also shows how detrimental the presence of a leak on the preconcentration system could be, as oxygen from a leak could cause the same phenomenon.

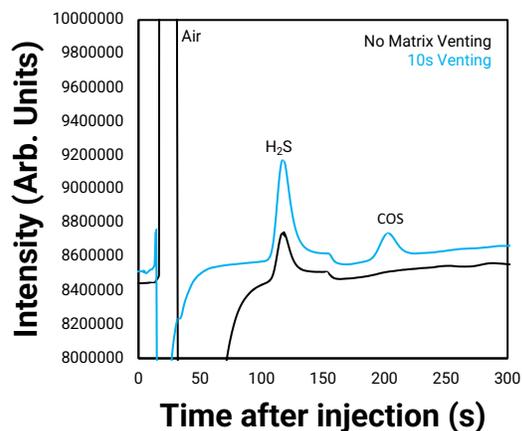


Figure 18 - Chromatograms acquired for 70.0 ppb H₂S and 66.8 ppb COS in air without matrix venting (Black Line) and with 10 seconds matrix venting (Blue Line)

This series of results highlights the importance of the matrix venting step. In other commercially-available thermal desorption systems, this would require at least two GC valves to do it. However, thanks to the unique design of the T&R PLSV used in ASDevices' SCS, this can all be done using a single valve without fearing for leak-integrity.

Signal Linearity

For precise quantification, it is essential to know the relation between the analyte concentration and the measured signal. For example, one of the main drawbacks of the FPD technology is its non-linearity. For the Epd technology, we have previously shown that the signal for the sulfur compounds is proportional to their concentration [10]. However, non-linearity could also come from the sample preconcentration system and the trapping material. This is why we characterized the response for the sulfur compounds once again, but using the SCS and our proprietary trapping material for sulfur compounds.

The following results were acquired with different H₂S, CS₂, MeSH, DMS and DMDS concentrations in hydrogen matrix. While we only present results acquired in hydrogen matrix, the same trends were also observed regardless of the matrix gas.

First, we determined the peak area as a function of concentration. As presented in Figure 19, a

linear relation, with a good R² between 0.99 and 0.9999 was obtained for all the compounds tested, from the low-ppb level, up to the tens of ppb, with at least 4 points for each compound. All the dilutions were obtained by mixing a standard gas sample containing the sulfur compounds with high-purity hydrogen using the iGCS system. Each gas flow was maintained in the sonic regime to insure precise dilution. The sampling flow rate was set to 150mL/min for 4 minutes at -30°C with 10 seconds matrix venting. The sample was released at 210°C. The setup for this test used the DB-Sulfur and GS-GasPro columns. A typical chromatogram acquired in those conditions is presented in Figure 12.

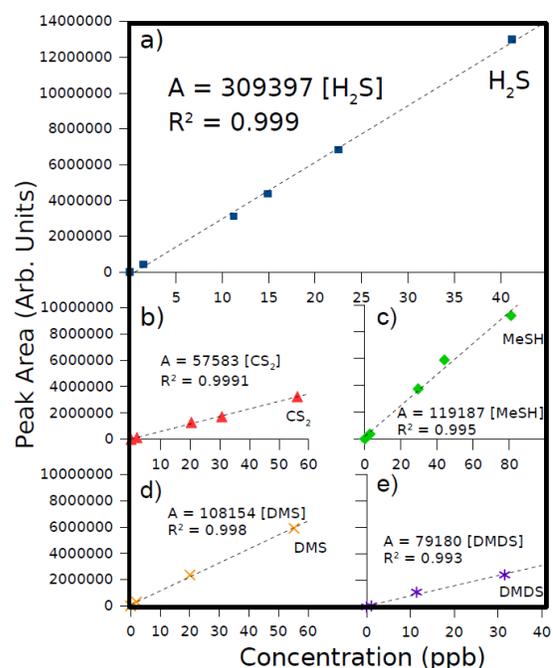


Figure 19 - Peak area as a function of concentration for a) H₂S, b) CS₂, c) MeSH, d) DMS and e) DMDS in hydrogen after 4 minutes sampling at 150mL/min and 10 seconds matrix venting

The response for each analyte as a function of the sampling volume was also tested, as presented in Figure 20. A concentration of 14.9 ppb for H₂S, 20.4 ppb for CS₂, 29.5 ppb for MeSH, 20.1 ppb for DMS and 11.4 ppb for DMDS was set using the iGCS and remained constant for the test. Only the sampling time was changed from 4 minutes to 8 minutes and 12 minutes. The relation between the peak intensity and sampling volume follows a

second-degree polynomial with a good R^2 above 0.999 for all the compounds tested. This was to be expected, as with the increasing sampling volume, the active sites of the trapping materials are progressively filled, eventually leading to a plateau. Still, for all the compounds, increasing the sampling volume up to 1800mL significantly increased the measured signal. Only DMS reached a plateau around this value. The same trend was observed with different sampling flow rates from 25 to 200mL/min. Therefore, the LOD for these compounds can be always be improved by increasing the sampling volume by increasing the sampling flow rate and/or increasing the sampling time. Note that thanks to the unique T&R PLSV design, the sampling step can be done while the chromatogram from the previous injection is being acquired. Therefore, the sampling time can be increased without increasing the whole cycle time.

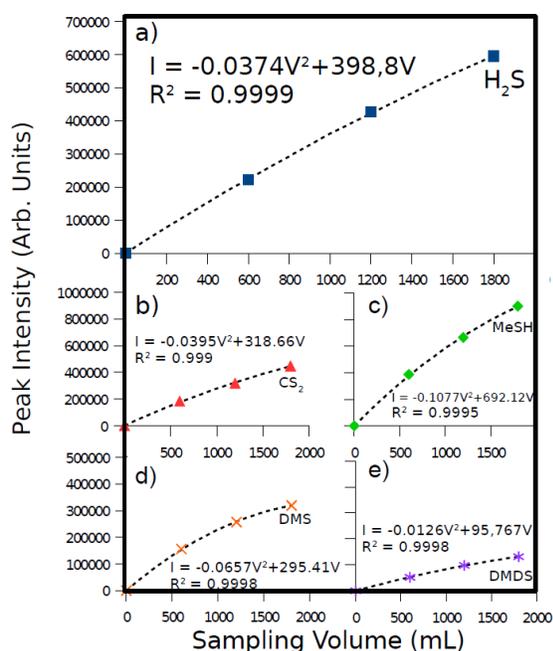


Figure 20 - Peak intensity as a function of the sampling volume for a) H₂S, b) CS₂, c) MeSH, d) DMS and e) DMDS in hydrogen with a sample flow rate of 150mL/min through the trap at -30°C

Conclusions

In conclusion, ASDevices' miniMOv GC platform, combined with the SCS and the Epd technology, was successfully used for the analysis of ultra-

trace level sulfur compounds in hydrogen, air and carbon dioxide. To generate such low-concentration sample, the iGCS was used to dilute standard samples containing approximately 50 ppm of various sulfur compounds down to a few ppb in these matrices. All the compounds were measured with LODs between 100 ppt and 300 ppt without using eLOD algorithm. With the eLOD algorithm, a LOD of 70 ppt should be expected for the reduced sulfur compounds. Furthermore, results acquired for 10 consecutive chromatograms of ultra-trace level sulfur compounds in hydrogen showed excellent repeatability. However, future works on trapping materials for COS and CS₂ in CO₂ will be needed.

The LODs presented in this document were obtained by preconcentrating 600mL of sample on ASDevices' proprietary trapping material. The linearity results showed that the signal for all the sulfur compounds can be significantly improved by sampling up to 1800 mL and possibly more. A good linearity for the peak area as a function of concentration was also observed for all the sulfur compounds. This demonstrates that such system could be used as an alternative to systems that use SCD and FPD.

The same results could also be obtained using ASDevices' process-oriented iMOv GC platform. Indeed, this platform use the same high-quality components and can be assembled with the same configuration for sulfur analysis. The SCS is also available in a rack-mount configuration compatible with this platform. Such performance for sulfur analysis with a process-oriented system has never been achieved previously and represents a groundbreaking achievement in the field.

Future Work

The present document focussed on results that were acquired using a "typical" GC configuration for sample preconcentration. Such configuration will always remain pertinent in laboratory as well as most process analysis. While the results presented here can only be achieved thanks to the high quality of all the components used in the SCS and miniMOv platform, as well as the new ASDevices' proprietary trapping material, the performance is still affected by intrinsic limitations of this traditional configuration, as the

trap remains inline with the chromatographic system (GC column and detector) when the sample is released. For example, the retention of the compounds in the trap can cause peak broadening, which has an effect on the LOD. The trap can also have an effect on the retention time of each peak, which can eventually drift in the long run. Furthermore, the trap is still susceptible to contamination by impurities from the sample such as heavy hydrocarbons. This could have a negative impact on the baseline or cause contamination of the GC columns, as the impurities can build-up on the trap and be slowly released when the trap is inline with the rest of the system.

While the current method is still excellent for sulfur preconcentration and measurement, it is not adapted for the preconcentration of many key impurities such as the permanent gases (H_2 , O_2 , N_2 , CH_4 , CO , CO_2), which require large and restrictive traps.

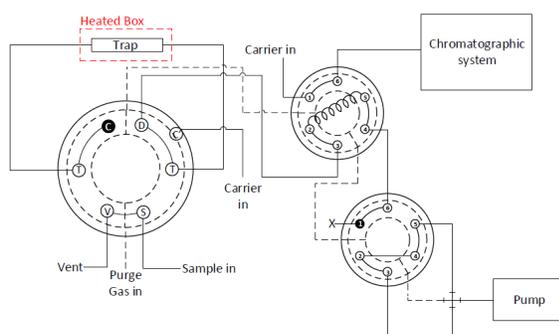


Figure 21 – New patent-pending method for preconcentration of the sample followed by injection through the chromatographic system from a sample loop.

In the past year, we developed a new patent-pending method for the preconcentration of these compounds, which is presented in Figure 21. Note that it is only an example of possible configuration and multiple variations are also possible. Regardless of the exact configuration, in this method, the content of a trap is released in a sample loop from a 6-ports PLSV injection valve. Once equilibrium is reached in the sample line, the preconcentrated sample that was released from the preconcentration system is injected through the chromatographic system by the injection valve. Since the sample is released

as a pulse and the trap is not directly inline with the rest of the chromatographic system, this new method is not affected by pressure swings, impurities bleeding or peak broadening caused by the trap. This new method also opens the possibility of using a preconcentration system located closer to the process, which would be safer for the analysis of highly flammable matrices like hydrogen.

In future works, we will focus on the development of a protocol for sulfur analysis that use this new preconcentration method. This will help to overcome the issues associated with the traditional configuration. Furthermore, it will be easier to use in combination with a system we already use for the preconcentration of permanent gases, which are also key impurities for multiple applications.

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